

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Stabilisation of Polyurethane Elastomers

5 We, TOYO SPINNING CO. LTD., a corporation of Japan, of No. 8, Dojima-Hamadori 2-chome, Kita-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a method for stabilising polyurethane elastomers and, more particularly, to a method for preventing the discolouration of polyurethane elastomers by contact with combustion gas or ultraviolet radiation.

15 Elastomers based on isocyanates, i.e. polyurethane elastomers, have the disadvantage of yellowing or being burnt (or browning) upon exposure to ultraviolet radiation, hydrocarbon and other combustion gases, or gaseous oxides of nitrogen.

20 In order to improve the resistance to weathering of polyurethane elastomers containing, for example, amino groups, imino groups, urea linkages, acid-amide linkages and urethane linkages, it is conventional to add antioxidants, ultraviolet absorbents or combustion gas discolouration inhibitors. Usually the ultraviolet absorbent is used together with the antioxidant and other stabilisers.

30 However, none of the many polyurethane elastomer stabilisers so far known afford fully satisfactory protection against ultraviolet radiation or gas discolouration, and many of them have failed completely to prevent the discolouration of polyurethane elastomers under long exposures to radiation or combustion gas of hydrocarbon fuels. Some of them rather detract from the desirable properties of polyurethane elastomers. Moreover, since the stabilising efficiency of the gas discolouration inhibiting or other stabilising agent depends on the compatibility or affinity between the particular agent and the particular polymer to

be stabilised, reactivity of the agent within the polymer and other factors, the choice of agent should be made with reference to the particular polymer. 45

We have found that the yellowing or burning (browning) of a polyurethane elastomer by the action of ultraviolet radiation or combustion gas is substantially prevented by adding at least one anhydride of a saturated aliphatic monocarboxylic acid to the polyurethane elastomer. 50

Thus, in accordance with the invention there is provided a method for stabilising a polyurethane elastomer which comprises adding or applying thereto at least one anhydride of a saturated aliphatic monocarboxylic acid. 55

The term "polyurethane elastomers" as used herein means any and all elastomers containing urethane linkages, urea linkages, or acid amide linkages. For example, they may be produced by reacting a polyglycol having terminal hydroxyl radicals with an excess of organic diisocyanate to prepare a prepolymer having terminal isocyanate radicals, and, then, extending the polymer chain with a bifunctional compound having active hydrogen atoms. 60

Since methods of producing these linear polyurethane elastomers by the above procedure are well known in the art and do not constitute part of the present invention, no further detailed explanation thereabout would be necessary except the following description which explains some preferable methods of producing polyurethane elastomers to which the present invention may be conveniently applied. 65

It is preferable to produce polyurethane elastomers by reacting an excess of an organic diisocyanate with a polyglycol to prepare a prepolymer having terminal hydroxy radicals, dissolving the prepolymer so prepared in a polar solvent, and reacting the prepolymer in the solution so prepared with a bifunctional 70

active hydrogen-containing compound to proceed the polymer chain extension or polymerisation. At the end of the polymerisation or chain extending reaction, it is sometimes preferable to stop the chain with a suitable chain stopper. Furthermore, in order to stabilise the viscosity of the resulting polymer solution, it is preferable to neutralise the excess of any remaining amine (used as the chain extender or chain stopper) with acid, which may typically be acetic acid.

Examples of preferred organic diisocyanates to be used in the production of polyurethane elastomers are those having aromatic rings, e.g. methylene-bis-(4-phenyl isocyanate), 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate and *m*-phenylene diisocyanate. More preferable are those diisocyanates wherein the two isocyanate radicals are equal in reactivity and are fairly high in reactivity. Examples of these diisocyanates are *p*-phenylene diisocyanate, *m*-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, methylene-bis-(4-phenyl diisocyanate), and xylene diisocyanate.

Polyglycols to be used in the production of polyurethane elastomers preferably have a molecular weight of 500 to 6000 and a melting point not higher than 60° C., and are preferably dihydroxy polyethers or dihydroxy polyesters, which may be known per se.

Examples of polar solvents in which the prepolymer is dissolved and in which the chain extending reaction is conducted are *N,N*-dimethylformamide, *N,N*-dimethylacetamide, tetrahydrofuran, dimethylsulphoxide or a mixture of any two or more thereof.

The chain extender or bifunctional active hydrogen-containing compound which is used for extending the polymer chain may be a diol, a diamine or hydrazine.

The chain stopper may be, for example a monoamine, a hydroxyamine, or a monohydric alcohol.

The polymer solution prepared as above may be shaped into various articles, such as fibres or films, or it may be used in various coating applications.

The important feature of this invention is to incorporate in or apply to the polyurethane elastomers or their shaped articles at least one anhydride of a saturated aliphatic monocarboxylic acid.

The elastomers to which the said compound is added or applied may be in any form. For example, it may be added to the elastomer itself or a solution thereof or a dispersion thereof in a suitable dispersion medium. Alternatively, the compound may be applied to fibres, films, or elastomeric products made therefrom or to articles coated with the polymer.

The anhydride of a saturated aliphatic monocarboxylic acid to be employed in this invention is preferably one containing from 1

to 9 carbon atoms in the aliphatic chain, e.g. acetic anhydride, valeric anhydride or caproic anhydride.

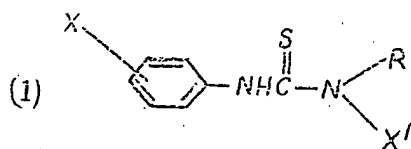
One of the preferred embodiments of this invention is to add the above-mentioned acid anhydride to a solution of the polymer.

If too much of the acid anhydride is used an excess of the acid anhydride would remain in the polymer composition. The excess anhydride will cause degradation of the polymer due to acid hydrolysis when the polymer composition contains or contacts water or other impurities. Therefore, the amount of the acid anhydride to be added or applied to the elastomer must be subject to the utmost scrutiny. Moreover, while the tendency of fibres and other shaped articles of polyurethane elastomers to yellow is substantially alleviated when they are after-treated with the acid anhydride, the articles may suffer somewhat in strength and other properties. This is presumably because, since it is relatively difficult to remove the excess of the acid anhydride adsorbed on the articles, the molecules forming the articles are hydrolyzed by the acid.

In another embodiment of this invention the anhydride of a saturated aliphatic monocarboxylic acid is applied to the fibres, films or other shaped article after they have been formed, e.g. at the time of oil treatment in the spinning process or in the course of after-treatment. However, in view of the possible removal of the said compounds upon repeated laundering, for instance, it is preferred to incorporate them in the polymer itself. The amount of the above-mentioned acid anhydride to be added or applied to the elastomer preferably ranges from 0.01% to 10%, and, more preferably, from 0.03% to 2% by weight based on the polyurethane elastomer, and from 3 to 20 mole % and, preferably, 8 to 12 mole % relative to the organic diisocyanate used in the preparation of the prepolymer. The addition of the acid anhydride is preferably made after the polymerisation reaction has gone to completion and, preferably, after the polymerisation is stopped, although it may also be added after the addition of acid for neutralisation. It is also possible to add the acid anhydride without adding the acid for the neutralisation.

In another preferred embodiment of the invention a *N*-phenylthiourea compound may be used in addition to the acid anhydride for stabilising the polyurethane elastomer. In this case, adequate stabilisation can be obtained even when the aggregate amount added is less than the sum of the optimum amounts of either used singly.

The *N*-phenylthioureas which are to be employed according to this embodiment of the invention are those compounds which may be represented by the general formula:



wherein X is a hydrogen atom or a halogen atom or an alkyl, aryl or aralkyl group, X' is a hydrogen atom or an alkyl, aryl or aralkyl group, and where X or X' contains a benzene ring, the said ring may be substituted with a halogen atom or an alkyl group having one to four carbon atoms, R is a hydrogen atom or an alkyl group containing one to four carbon atoms.

Thus, X may be exemplified by hydrogen, methyl, ethyl, propyl, tertiary butyl, benzyl, phenyl, chlorine, bromine and iodine. Among those represented by X' are, for example, hydrogen, methyl, ethyl, propyl, normal butyl, pentyl, phenyl, chlorophenyl, dichlorophenyl, biphenyl, benzyl and phenetyl, and R is exemplified by hydrogen, methyl, ethyl, propyl and *n*-butyl.

Examples of the compound having the above general formula (I) are N - phenylthiourea, N - 4 - methylphenyl - thiourea, N - phenyl - N' - methylthiourea, N - phenyl - N' - ethylthiourea, N - phenyl - N',N' - diethylthiourea, N,N' - diphenylthiourea, N-phenyl - N' - benzyl - thiourea, N,N' - di-(4 - methylphenyl)thiourea, N - phenyl - N' - methyl - N' - phenylthiourea, N - 4 - chlorophenyl - N' - phenylthiourea, N - 2 - chlorophenyl - N' - phenylthiourea, N,N' - di - (4 - chlorophenyl) - thiourea, N,N' - di - (4 - bromophenyl) - thiourea, N - 4 - bromophenyl - N' - phenylthiourea and N - phenyl - N' - (4 - ethylbenzoate) - thiourea.

Our Application No. 7607/65 (Serial 1,095,921) describes and claims a method for stabilising a polyurethane elastomer which comprises adding or applying thereto at least one N-phenylthiourea.

By the incorporation or application of the acid anhydride or the acid anhydride and N-phenylthiourea to a polyurethane elastomer according to this invention the elastomer and articles made therefrom are stabilised against development of colour by the action of ultraviolet radiation and fumes or combustion gas.

To test the tendency of the polyurethane elastomer to be discoloured upon contact with combustion gas, a gas burner is placed in a container which has a capacity of 0.5m³ and the top wall of which is provided with a circular vent hole measuring 8 cm. in diameter, and the temperature within the container is held at 60°C. by allowing the burner to effect complete combustion of 800 c.c. of propane gas per minute. The concentration of nitrogen dioxide (NO₂) gas within the container is 0.74 × 10⁻⁶ g/l. The specimen to be tested is

suspended within the containers so that it remains exposed to the combustion gas or fume for 5 hours, at the end of which time the specimen is taken out and graded. Grade 1 corresponds to the polyurethane elastomer containing no stabiliser, which has been severely discoloured by the gas. Grade 5 is equivalent to the colour of the polyurethane elastomer which has not been exposed to the gas. Between the two grades, there are three grades to classify the degree of discolouration.

To ascertain the resistance of the polyurethane elastomer to ultraviolet radiation a "Fade-O-Meter" is used. The word "Fade-O-Meter" is a registered Trade Mark. The specimen placed at a distance of 25 centimeters from a source of ultraviolet radiation, 1400 V, 17 A, is irradiated at an ambient temperature of 40°C. Based on the results obtained, the specimen is graded. Grade 1 corresponds with the polyurethane elastomer containing no stabiliser, which has been severely discoloured. Grade 5 is equivalent to the colour of the polyurethane elastomer which has not been exposed to radiation. Between the two extremes, there are three grades.

When the acid anhydride is used alone as the stabiliser according to the invention, there are observed improvements in the resistance of the polyurethane elastomer to both ultraviolet and gas discolourations and the results of the above-mentioned two tests correspond to Grade 3 or better.

To fully exploit these favourable effects, it is particularly desirable to add or apply the anhydride of a saturated aliphatic monocarboxylic acid together with a N-phenylthiourea compound to polyurethane elastomers.

This invention will be further described in detail by way of the following Examples, in which all parts are by weight unless otherwise specified.

EXAMPLE 1.

To a prepolymer prepared from 500 parts by methylene-bis-(4-phenylisocyanate) and 1150 parts of polyoxytetramethylene ether glycol (average molecular weight: 1150) were added 10 parts of 4,4' - butylidene - bis(6-*t* - butyl - *m* - cresol), 8 parts of 2 - (2-hydroxy - 5 - methylphenyl)benzotriazole and 60 parts of zinc sulphide (average grain diameter: 0.3μ). Then the prepolymer was dissolved in dimethylformamide and subjected to chain-extension by the addition of 67 parts of 1,2-propylene diamine. When the viscosity of the solution reached 1500 poise, the above reaction was stopped by the addition of 6 parts of monomethanolamine, followed by the addition of 3 parts of acetic acid to neutralise the excess amine. Then 10 parts of acetic anhydride were added to the above solution, which was thoroughly stirred. The polymer solution prepared as above was heated to 100° C. and extruded through a spinnerette

- having 30 holes (each 0.2 mm. in diameter) in a dry-spinning column. The filaments taken out from the column were passed over a moving roll partially submerged in a soap slurry and taken up at the rate of 290 m/min. The soap slurry used above was an aqueous dispersion prepared by dispersing calcium stearate in an oily preparation composed mainly of mineral oil and non-ionic surfactant, the concentration of calcium stearate being 30 to 60 g/l. The filaments prepared above were treated with water vapour at 100° C. for 30 minutes, followed by drying at 80° C. for 3 hours. The resistance of the resulting elastic yarn to weathering was as follows. The sample was irradiated with ultraviolet radiation by a "Fade-O-Meter" and the changes in strength and degrees of discolouration of the samples were measured. As a control, the table also shows the result sfor a similar elastic yarn prepared from a solution which was the same as above but containing no acetic anhydride.

	Acetic anhydride added		No acetic anhydride	
	Strength	Whiteness	Strength	Whiteness
Not irradiated	0.89g/d	Grade 5	0.85g/d	Grade 5
"Fade-O-Meter" 60 hours	0.89g/d	Grade 4	0.80g/d	Grade 3
After gas discolouration test		Grade 3		Grade 2

EXAMPLE 2.

- A polyurethane solution was prepared in the same manner as in Example 1, except that acetic anhydride was replaced with 20 parts of propionic anhydride, and 20 parts of butyric anhydride, respectively. Each polymer solution was spun into elastic yarn in the same manner as in the preceding Example. These elastic yarns were exposed to combustion gas in the described manner. The results are summarized below.

- | | |
|---------------------|---------|
| Propionic anhydride | Grade 3 |
| Butyric anhydride | Grade 3 |

EXAMPLE 3.

- To 10 parts of methylene - bis - (4-phenyl - isocyanate) was added 0.45 part of 4,4' - butylidene - bis - (6 - t - butyl - m-cresol), followed by the addition of 23 parts of polytetramethylene ether glycol (average molecular weight: 1000). The mixture was allowed to react to obtain a prepolymer.

Then, 0.9 part of zinc sulphide (average grain diameter: 0.3 μ) and 0.3 part of chlorine-substituted 2 - (2 - oxy - 5 - hexylphenyl)-benzotriazole were added. While stirring the mixture vigorously, 1,2-propylene diamine and, then, 0.35 part of acetic anhydride were added. The concentration of the polymer was 25%. This solution was extruded through a spinnerette having 30 holes (each 0.1 mm. in diameter) into an ethylene glycol bath at 85° C. and the filaments were taken up at the rate of 30 m/min. The resulting filaments were held under 50% tension and immersed in boiling water at 100° C. for 30 minutes, followed by drying. The elastic yarn prepared as above was irradiated with ultraviolet radiation to determine its weather resistance. As a control, a similar elastic yarn which had been prepared in the same manner as above except that acetic anhydride had been replaced with 0.35 part of acetic acid was also tested. The results are summarized below.

	Acetic anhydride added		No acetic anhydride	
	Strength	Whiteness	Strength	Whiteness
Not irradiated	0.65g/d	Grade 5	0.67g/d	Grade 5
"Fade-O-Meter" 60 hours	0.64g/d	Grade 4	0.85g/d	Grade 3
After gas discolouration test		Grade 3		Grade 2

It will be apparent from the above table that the elastic yarn containing acetic anhydride is superior to the yarn containing acetic acid in weather resistance.

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EXAMPLE 4.

To a prepolymer prepared from 750 parts of methylene - bis - (4 - phenylisocyanate) and 2300 parts of polytetramethylene-ether glycol (average molecular weight: 1150) were added 30 parts of 4,4' - isopropylidene-bis - (6 - *t* - butyl - *m* - cresol), 25 parts of 2(2 - oxy - 5-methylphenyl) - benzotriazole, and 60 parts of zinc sulphide (average grain diameter: 0.3 μ). The prepolymer was then dissolved in dimethylformamide and was subjected to chain extension by adding 67 parts

of 1,2-propylene diamine. When the viscosity of the solution reached 1000 poise, the reaction was stopped by adding 10 parts of monoethanolamine, followed by the addition of 3 parts of acetic acid to neutralise the excess amine. Then, the solution was heated and dry-spun in an atmosphere of 250° C. The filaments were immersed in an acetic anhydride bath at 700° C. for about 30 seconds, washed with water, and dried at 80° C. for 60 minutes. The resistance of the elastic yarn prepared as above to ultraviolet radiation was as follows. The table also shows the results for a similar elastic yarn which had been prepared in the same manner as above but had not been treated with acetic anhydride.

	Elastic yarn of this invention		No acetic anhydride	
	Strength	Whiteness	Strength	Whiteness
Not irradiated	0.69g/d	Grade 5	0.70g/d	Grade 5
"Fade-O-Meter"	0.57g/0	Grade 4	0.58g/d	Grade 3

It will be apparent from the above table that the elastic yarn treated with acetic anhydride according to this invention is more resistant to ultraviolet discoloration. Since the treatment of the filament with 100% acetic anhydride is rather severe, it was suspected that the filament might be damaged and its strength affected, but as it turned out, no appreciable difference was observed between the filament and a similar filament which was not treated with acetic anhydride.

EXAMPLE 5.

Five moles of diethyl adipate, 10 moles of ethylene glycol, and 0.01 mole of zinc acetate were mixed together and an ester exchange was conducted at 170° C. After the ethanol was distilled out, the temperature was increased to 240° C. and heating was continued under reduced pressure until a predetermined amount of ethylene glycol was distilled out (about 5 hours) whereupon polyester glycol having an acid value of 0.4 and a hydroxy value of 77 was obtained. 290 parts of this polyester glycol were reacted with 100 parts of diphenylmethane 4,4'-diisocyanate at 90° C. for 40 minutes to prepare a prepolymer. 60 parts of the prepolymer obtained as above was dissolved in 150 parts of N,N-dimethylformamide, and the solution cooled to 0° C. Then, a solution of 3 parts of 1,2-propylene diamine in 50 parts of N,N-dimethylformamide was gradually added with continued stirring until the viscosity of the solution reached 1200 poise. At this time, di-

butylamine and, then, 0.6 part of acetic anhydride were added, followed, further, by the addition of 0.7 part of N,N'-diphenylthiourea with stirring. The mixture was then adjusted to room temperature and extruded through a spinnerette having 10 holes into a dry-spinning column held at 180° C. The filaments were taken up just below the spinning column.

When the resistance of the resulting polyurethane elastic yarn to combustion gas was measured as above, it was found to correspond to Grade 4 — 5.

A similar polyurethane elastic yarn prepared in the same manner as above except that no N,N'-diphenylthiourea had been added was found to be equivalent to Grade 3 in the same test.

EXAMPLE 6.

Forty parts of polytetramethylene-ether-glycol (average molecular weight: 1000) was reacted with 20 parts of methylene-bis-(4-phenyl-isocyanate) at 80° C. for one hour with constant stirring to prepare a prepolymer having terminal isocyanate radicals, which was dissolved in 100 parts of N,N-dimethylformamide. The reaction mixture was stirred for 15 minutes while cooling with water, and then a solution of 1.8 parts of hydrazine hydrate in 50 parts of N,N-dimethylformamide was gradually added. The viscosity of the resulting solution was 2800 poise at 20° C. The polymerisation reaction was stopped by adding 3 parts of a 10% solution of monoethanol amine

in N,N-dimethylformamide to the above reaction mixture.

- To 100 parts of the resulting solution was added 0.3 part of 2 - (2 - hydroxy - 5-methylphenyl)benzotriazole (ultraviolet absorbent) and 0.3 part of 4,4' - butylidenebis - (6 - *t* - butyl - *m* - cresol) (antioxidant) and the mixture was thoroughly stirred to prepare a solution. To each 10 parts of this solution was added 0.05 part of N-phenyl - N',N' - diethylthiourea, N - *o*-chlorophenyl - N' - phenylthiourea, N,N'-

di - (*p* - chlorophenyl) - thiourea, and N,N'-di - *p* - tolylthiourea, respectively.

To each of these four spinning solution was added 0.05 part of acetic anhydride and the resulting solutions were extruded through a spinnerette having 14 holes into a dry-spinning column held at 220° C. and the resulting filaments were taken up at the rate of 200 m/min. The resulting polyurethane elastic yarns were exposed to ultraviolet radiation for 40 hours by means of a "Fade-O-Meter".

	"Fade-O-Meter" 40 hr.
N-phenyl-N',N'-diethylthiourea	Grade 4
N- <i>o</i> -chlorophenyl-N'-phenylthiourea	Grade 4 — 5
N,N'-di-(<i>p</i> -chlorophenyl)-thiourea	Grade 4 — 5
N,N'-di- <i>p</i> -tolylthiourea	Grade 4

WHAT WE CLAIM IS:—

1. A method for stabilising a polyurethane elastomer which comprises adding or applying thereto at least one anhydride of a saturated aliphatic monocarboxylic acid.

2. A method according to claim 1, wherein the aliphatic monocarboxylic acid contains from 1 to 9 carbon atoms in the aliphatic chain.

3. A method according to either one of claims 1 or 2, wherein the anhydride is acetic anhydride.

4. A method according to any one of claims 1 to 3, wherein the amount of anhydride ranges from 0.01 to 10% by weight based upon the polyurethane elastomer.

5. A method according to claim 4, wherein the amount of anhydride ranges from 0.03 to 2% by weight based upon the polyurethane elastomer.

6. A method according to any one of the preceding claims, wherein the anhydride is added or applied together with at least one N-phenylthiourea compound.

7. A method according to any one of the preceding claims, wherein the anhydride, or the anhydride and the N-phenylthiourea compound, is added to a spinning solution of polyurethane elastomer.

8. A method according to any one of claims 1 to 6, wherein the anhydride, or the anhydride and the N-phenylthiourea compound, is applied to elastic yarns of polyurethane elastomer.

9. A method for stabilising a polyurethane elastomer according to claim 1 and substantially as hereinbefore described with reference to the Examples.

10. Polyurethane elastomers and fibres, films and articles made therefrom wherever stabilised by the method according to any one of the preceding claims.

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